

# ✿ Polyoxyethylene Oligomer Distribution of Nonionic Surfactants

Takatoshi Sato<sup>a</sup>, Yoshihiro Saito<sup>a</sup> and Ichiro Anazawa<sup>b</sup>

<sup>a</sup>Department of Pharmacy, College of Science and Technology, Nihon University, 8, Kanda Surugadai, 1-Chome, Chiyoda-ku, Tokyo, Japan and <sup>b</sup>Department of Industrial Chemistry, College of Industrial Technology, Nihon University, Chiba, Japan

Thin layer chromatography with a flame ionization detection (TLC-FID) technique was applied to the separation and determination of nonionic surfactants containing oxyethylene (OE) chains. The OE adducts with an average number of 4.2, 6.0 and 8.0 oxyethylene units were separated on Chromarod S-II (Silica gel-coated rods) with double development using benzene:ethyl acetate (6:4) and ethyl acetate:acetic acid:water (8:1:1). OE adducts of nonionic surfactants were well separated by the TLC-FID method using simple and standard techniques that eliminate the need for any chemical modification.

Nonionic surfactants containing polyoxyethylene chains are important surfactants used commercially for many years as emulsifiers and solubilizers. Also, it is reported that the distribution of the oxyethylene (OE) chains affects various surface chemical properties, such as foaming, wetting and emulsification (1). Therefore, knowledge of the distribution of OE chain is important, and many studies on its analysis by means of column chromatography and TLC have been reported, but they are not convenient for routine work (2-3). Although gas chromatographic (GC) methods are also available and can be carried out more easily and rapidly than previous chromatographic methods, GC methods cannot be applied to nonionic surfactants containing long OE chains (4-5). Recently, several attempts at separation and quantitative estimation of nonionic surfactants containing OE chains by high performance liquid chromatographic (HPLC) methods have been reported. However, HPLC methods also seem to be inconvenient for routine work because the UV detector used in HPLC normally is limited to poly(OE) alkyl phenols. Other nonionic surfactants containing OE chains need chemical modification in order to use all detector (6-7).

TLC-FID recently was shown to be useful in analyzing lipids and phospholipids from different sources (8). Also, we have reported previously the analysis of an anionic surfactant in an ointment using TLC-FID (9). In this work we used the method to determine the distribution of OE chains of nonionic surfactants.

## EXPERIMENTAL

**Materials.** The nonionic surfactant samples, polyoxyethylene monododecyl ethers (POED-n, n = 4.2, 6.0 and 8.0, where n is the average number of the OE chains), were obtained from Nikko Chemicals Co. Ltd. and Kao Chemicals Co. Ltd. These nonionic surfactants were purified in accordance with our previous paper (10). Surfactant samples each having one single poly(OE)

chain length (OE = 1 through 8) were prepared from homogeneous poly(OE) monododecyl ethers (Nikko Chemicals Co. Ltd.). The purity was found by GC to be in excess of 98.0%. Other reagents were extra pure grade and were used without further purification.

**Procedures.** A summary of the analytical conditions by TLC-FID is shown in Table 1. The studies of the distribution of OE chains by TLC methods (11-12) used silica gel-coated plate and were a good guide to the selection of development solvents for TLC-FID, because Chromarod-SII is done with silica gel-coated rods. For the preparation of the samples, the POED-n were dissolved in acetone (concentration of 10 mg/ml). One  $\mu$ l of the POED-n solution was applied to silica gel-coated rods. The rods were dried and then developed in solvent containing benzene:ethyl acetate (6:4, v/v) to a distance of 10 cm from the point of application. The rods were dried thoroughly with a hair dryer, and then developed in solvent containing ethyl acetate:acetic acid:water (8:1:1) to a distance of seven cm for POED-4.2 and nine cm for both POED-6.0 and POED-8.0 from the point of application.

After development, solvent on the rods was removed and the rods were passed through a FID. A digital integrator (Shimadzu Co., Model C-R1B) was used for the calculation of the peak areas.

## RESULTS AND DISCUSSION

Typical TLC-FID chromatograms obtained for POED-n are shown in Figures 1-3. A satisfactory separation of 11-14 peaks was made using the present method. Identification of the peaks in Figures 1-3 was made using standard samples prepared from pure poly(OE) monododecyl ethers. As a result, it was clear that the peaks were detected in order of the OE chain length. Ordinarily, OE = 0 and OE = 1 peaks are integrated together. However, it is possible to estimate the relative amounts of OE = 0 and OE = 1 present, because the OE = 0, 1 peaks were separated completely by shortening the distance of the second development to six cm.

TABLE 1

### Summary of Analytical Conditions by TLC-FID

Apparatus:	Iatron TH-10 (Iatron Co., Ltd., Japan)
Stationary phase:	Chromarod-SII (Silica gel-coated rod)
Mobile phase:	1st development, Benzene:ethyl acetate (6:4), 10 cm 2nd development, Ethyl acetate:acetic acid:water (8:1:1), 7 cm for POED-4.2, 9 cm for POED-6.0 and POED-8.0
Gas flow:	H <sub>2</sub> , 160 ml/min; air, 2 l/min
Scanning speed:	35 sec/scan
Chart speed:	100 mm/min

\*To whom correspondence should be addressed.

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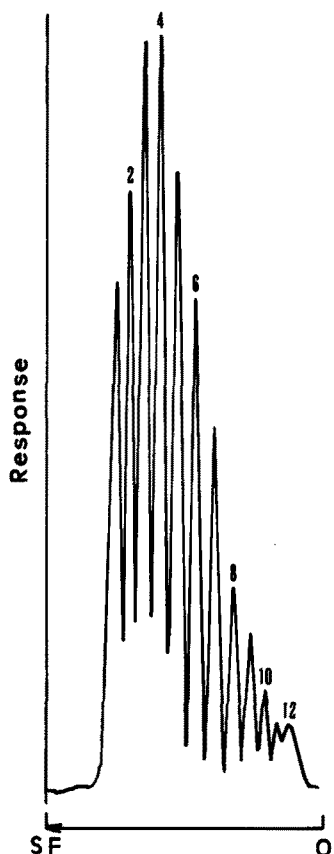


FIG. 1. TLC-FID chromatogram of POED-4.2. The peak number corresponds to the number of OE chains. SF, solvent front; O, origin.

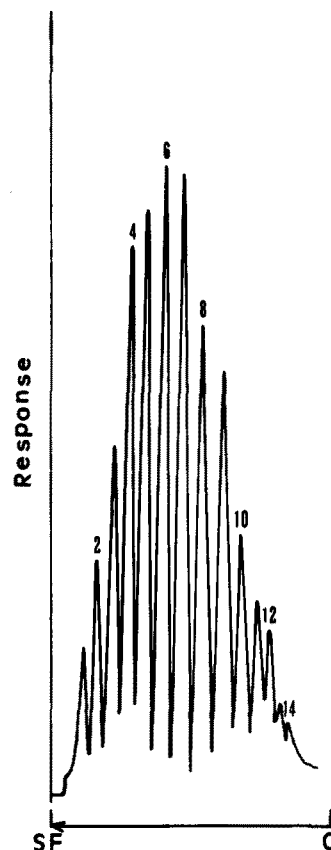


FIG. 3. TLC-FID chromatogram of POED-8.0.

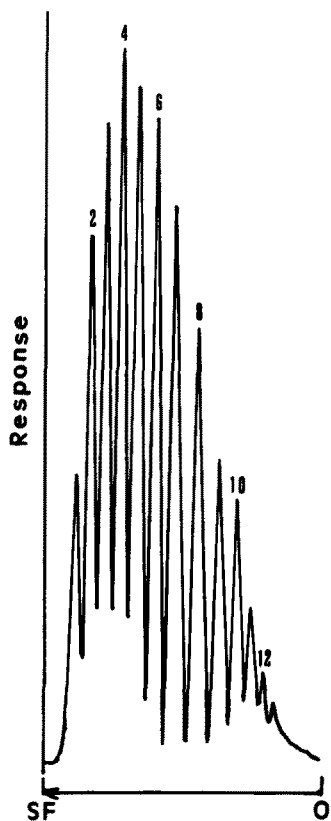


FIG. 2. TLC-FID chromatogram of POED-6.0.

From the original chromatogram, it was estimated that the OE = 0, 1 peaks contained 33.5% OE = 0 for POED-4.2, 26.5% OE = 0 for POED-6.0 and 42.9% OE = 0 for POED-8.0.

Because the areas of the peaks obtained from Figures 1-3 are relative, they were corrected by the calculation of response factors for each OE chain of the FID. Response factors have been determined by TLC-FID analyses of equal weights of homogeneous poly(OE) monododecyl ethers having one single OE chain length. As pure materials with OE more than eight were not commercially available, response factors for them could not be determined experimentally. However, plotting response factors for OE = 0 through OE = 8 gave a linear curve, against OE chain length, and so response factors for OE > 8 were calculated by means of extrapolation.

Tables 2-4 show the response factors, molar distribution, weight distribution and analytical precision of POED-n by the TLC-FID method. Figures 4-6 depict the distribution determined from the samples given in Tables 2-4. The largest peaks in the case of POED-4.2 are those having 2-6 OE chains. In POED-6.0, the main components contained 2-8 OE chains, whereas the main ones in POED-8.0 were those containing 4-9 OE chains.

From these results, it was calculated that an average molecular weight was 361.1 (OE number = 4.0) for POED-4.2, 414.4 (OE number = 5.2) for POED-6.0 and 462.7 (OE number = 6.3) for POED-8.0. A sample of POED-6.0 was analyzed by Nozawa and Ohnuma (7)

TABLE 2

OE Distribution and Statistical Analysis of POED-4.2 (n = 4)

OE no.	Relative response factors	Molar distribution	Weight distribution	% SD/X
0	0.95	0.0569	0.0293	4.9
1	1.00	0.0961	0.0612	4.3
2	1.08	0.1582	0.1201	8.7
3	1.15	0.1664	0.1466	7.1
4	1.23	0.1580	0.1584	2.7
5	1.35	0.1166	0.1311	7.6
6	1.47	0.0892	0.1112	7.1
7	1.60	0.0646	0.0884	9.6
8	1.82	0.0383	0.0571	9.8
9	2.03	0.0263	0.0424	9.9
10	2.30	0.0132	0.0229	12.3
11	2.72	0.0064	0.0118	15.3
12	3.29	0.0099	0.0195	10.2

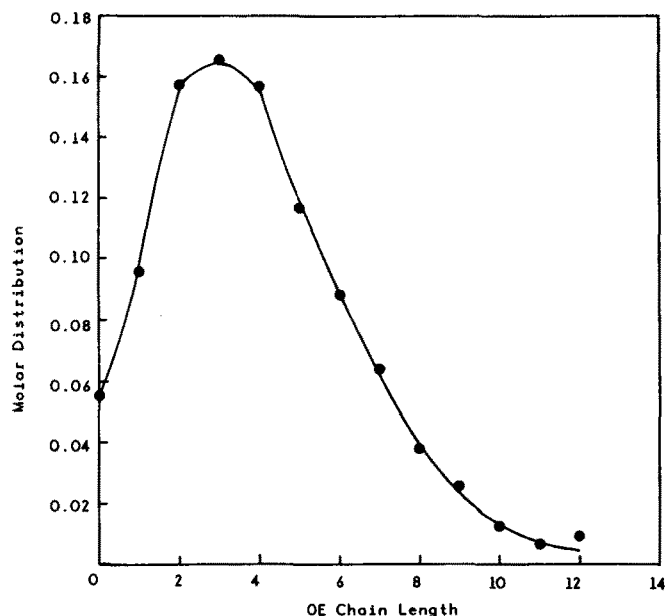


FIG. 4. Molar distribution of POED-4.2.

TABLE 3

OE Distribution and Statistical Analysis of POED-6.0 (n = 4)

OE no.	Relative response factors	Molar distribution	Weight distribution	% SD/X
0	0.94	0.0243	0.0109	6.2
1	1.00	0.0578	0.0321	10.1
2	1.05	0.1113	0.0736	8.1
3	1.13	0.1248	0.0958	1.7
4	1.21	0.1310	0.1145	1.6
5	1.31	0.1180	0.1156	2.2
6	1.41	0.1103	0.1198	5.8
7	1.54	0.0995	0.1186	4.2
8	1.68	0.0818	0.1062	12.8
9	1.88	0.0594	0.0835	12.9
10	2.13	0.0446	0.0674	3.3
11	2.42	0.0227	0.0367	6.7
12	2.79	0.0098	0.0169	17.3
13	3.37	0.0047	0.0086	19.1

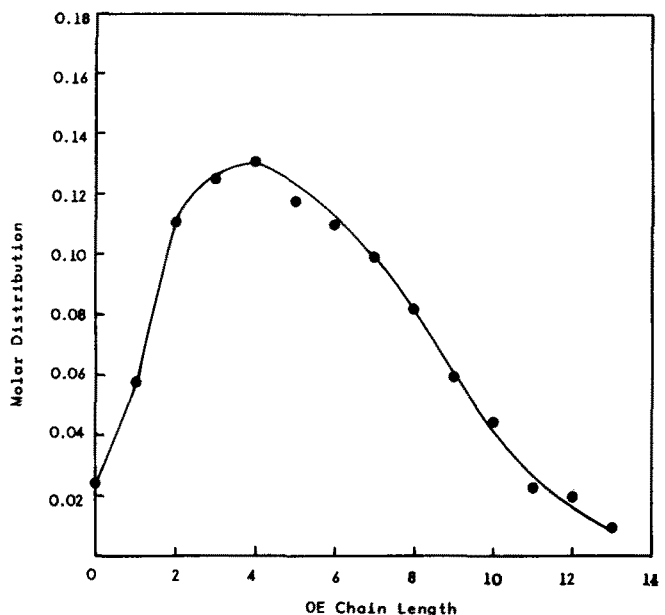


FIG. 5. Molar distribution of POED-6.0

TABLE 4

OE Distribution and Statistical Analysis of POED-8.0 (n = 4)

OE no.	Molar distribution	Weight distribution	% SD/X
0	0.0246	0.0099	6.7
1	0.0282	0.0140	15.4
2	0.0539	0.0319	10.8
3	0.0771	0.0530	14.2
4	0.1088	0.0851	4.4
5	0.1133	0.0994	2.7
6	0.1230	0.1196	8.2
7	0.1243	0.1327	6.5
8	0.1095	0.1273	1.3
9	0.0976	0.1228	2.4
10	0.0573	0.0775	17.2
11	0.0369	0.0534	18.6
12	0.0250	0.0385	19.5
13	0.0099	0.0163	22.8
14	0.0107	0.0185	17.6

using HPLC of esterified derivatives. A comparison of the TLC-FID analysis with the HPLC analysis of the POED-6.0 is presented in Table 5; the data shown are molar distribution. The agreement is excellent, but the HPLC method takes more time due to the esterification step with 3,5-dinitrobenzoyl chloride.

We believe the TLC-FID method is better than GC and HPLC methods in terms of simplicity and speed, because the TLC-FID method does not require chemical modification and can detect one sample in 35 seconds. This method may be used as an on-line technique for other surfactants as well, and give a better idea of the

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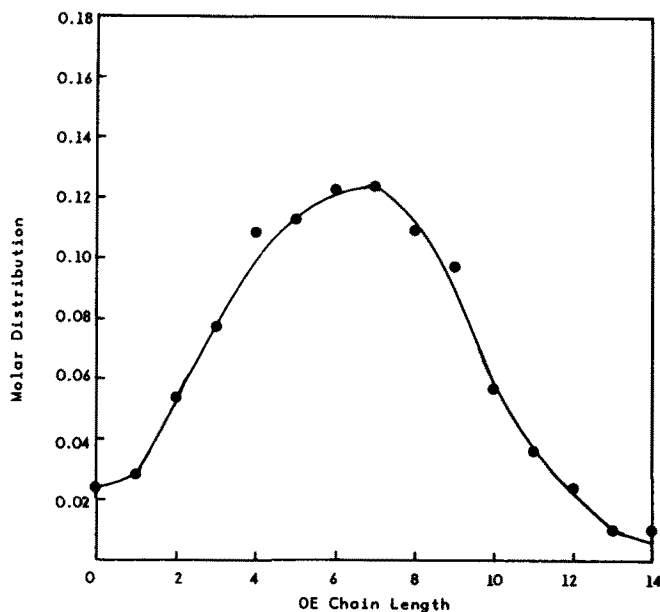


FIG. 6. Molar distribution of POED-8.0.

TABLE 5

Comparison of TLC-FID and HPLC Analyses of POED-6.0

OE no.	TLC-FID	HPLC
0	0.0243	0.0611
1	0.0578	0.0545
2	0.1113	0.0785
3	0.1248	0.1041
4	0.1310	0.1182
5	0.1180	0.1149
6	0.1103	0.1058
7	0.0995	0.0926
8	0.0818	0.0777
9	0.0594	0.0628
10	0.0446	0.0488
11	0.0227	0.0364
12	0.0098	-
13	0.0047	-

distribution in nonionic surfactants containing poly(OE) chains. However, the analysis by the TLC-FID method of nonionic surfactants containing longer OE chains is difficult. Therefore, we are attempting to establish a satisfactory TLC-FID method for determining longer poly(OE) chains.

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